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Advancements in time-resolved x-ray laser induced time-of-flight photoelectron spectroscopy

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ABSTRACT

Time-resolved soft x-ray photoelectron spectroscopy is used to probe the non-steady-state evolution of the valence band electronic structure of laser heated ultra-thin (50 nm) metal foils and bulk semiconductors. Single-shot soft x-ray laser induced time-of-flight photoelectron spectroscopy with picosecond time resolution was used in combination with optical measurements of the disassembly dynamics that have shown the existence of a metastable liquid phase in *fs*-laser heated metal foils persisting 4-5 ps. This metastable phase is studied using a 527 nm wavelength 400 fs laser pulse containing 0.3 – 2.5 mJ laser energy focused in a large 500 x 700 μm^2 spot to create heated conditions of $0.2 - 1.8 \times 10^{12} \text{ W cm}^{-2}$ intensity. The unique LLNL COMET compact tabletop soft x-ray laser source provided the necessary high photon flux, highly monoenergetic, picosecond pulse duration, and coherence for observing the evolution of changes in the valence band electronic structure of laser heated metals and semiconductors with picosecond time resolution. This work demonstrates the continuing development of a powerful new technique for probing reaction dynamics and changes of local order on surfaces on their fundamental timescales including phenomena such as non-thermal melting, chemical bond formation, intermediate reaction steps, and the existence of transient reaction products.

Keywords: time-of-flight photoemission, x-ray laser

1. INTRODUCTION

The application of compact high efficiency collisional excitation x-ray lasers operating with higher repetition rate pumps [1–4] for probing dynamical changes of matter with ultrafast time resolution has come of age. At Lawrence Livermore National Laboratory (LLNL) we have been developing time-of-flight techniques for photoelectron spectroscopy induced by single-shot x-ray laser pulses in a pump-probe investigation of changes in the electronic structure of materials undergoing ultrafast laser heating [5,6].

Time-of-flight (ToF) photoelectron spectroscopy (PES) with a pulsed synchrotron radiation source was first investigated as a means to determine energy and angular distributions in low photon energy regimes. [7] Other researchers have used ToF to observe static chemical shifts in the Si 2*p* core level electronic structure for SiO₂ and Si₃N₄ samples using 2.5 ns laser produced plasma (LPP), 255 eV x-ray pulses after integrating for ~100 shots [8,9]. These studies while successful have several significant limitations which rule out a pump-probe experiment to study dynamic processes in a material induced by shocks, e.g. melting, phase changes. Specifically, the low photon fluxes $\sim 2.5 \times 10^8$ photons/pulse on the sample required multiple shots to record a photoelectron spectrum. In addition, low x-ray source energy resolution, $\Delta E/E \sim 1.4 \times 10^{-2}$, and long 2.5 ns pulse duration limited the energy resolution of the photoelectron spectrum and therefore the ability to distinguish fine details in the electronic structure. Finally, time resolved observation of changes in the electronic structure during dynamic processes requires pulse durations on the order of a picosecond.

Higher order harmonic (HOH) sources overcome the limitations of the LPP sources and have the advantage of shorter pulse duration, e.g. less than 60 fs, at a high repetition rate [10-12] which makes them very attractive for dynamic pump-probe experiments. However, the presence of multiple harmonics requires further wavelength selection with multilayers or diffraction gratings. In addition, the lower photon fluence/shot requires many shots to achieve good signal statistics. Thus the need for monochromatic, high photon fluence, short pulse x-ray source for performing time-resolved dynamic studies.

Time-resolved core-level photoelectron spectroscopy performed at the Advanced Light Source has probed both the local arrangement of atoms (providing spatial information) as well as the bonding character of the valence electrons

(providing electronic information). [13] In these experiments, the total elapsed time from laser heating to final ejected particle formation was less than 100 ps and the results indicated that in the intermediate phase there is a metallic fluid where the electrons become mobile. The mobile electrons efficiently screen the x-ray core-hole leading to a *lowering* of the binding energy. The spectral modifications in this phase are due to the fact that core-level photoelectron spectroscopy is responsive to the character of the valence electronic wavefunction.

Each of the aforementioned studies with the different sources has their associated strengths and weaknesses. We will show that the LLNL COMET (Compact Multipulse Terawatt) x-ray laser, which is highly monochromatic with a combination of high photon fluence and ps pulse duration, is ideal to perform dynamic optical pump-x-ray probe electronic structure measurements on a single-shot. This paper presents results that demonstrate this capability.

2. EXPERIMENTAL

The experiments were performed on the COMET laser system at LLNL [2]. This laser, operating at 1054 nm wavelength, utilizes the technique of chirped pulse amplification to produce two high power beams at a rate of 1 shot every 4 minutes. A short pulse nominally 500 fs to 25 ps and a long 600 ps (FWHM) pulse is focused in a high intensity line focus with a traveling wave geometry to generate the Ni-like Pd ion $4d - 4p$ x-ray laser line at 14.7 nm (84.5 eV). Total energy in the two beams is of order 3 – 7 J to produce lasing where the peak-to-peak delay between the laser pulses is found to be optimal at 700 ps with the short pulse arriving after the long pulse. High photon flux/shot, high monochromaticity, and short pulse duration when combined with small source area and beam divergence properties of the 14.7 nm line [14] give ultra-high peak brightness $\sim 10^{25}$ ph. mm⁻² mrad⁻² s⁻¹ (0.1% BW)⁻¹ assuming a 2 ps pulse duration. Overall, the 14.7 nm peak brightness is 5 – 6 orders of magnitude higher than 3rd generation synchrotron undulator sources. However, third generation synchrotron undulator sources still have higher average brightness of $0.5 - 6 \times 10^{18}$ ph.mm⁻² mrad⁻² s⁻¹ (0.1% BW)⁻¹ at 50 – 10 nm, respectively. The technique of electron time-of-flight (e-ToF) spectroscopy requires a monochromatic, ps pulsed source for efficient x-ray laser induced photoelectron spectroscopy (PES).

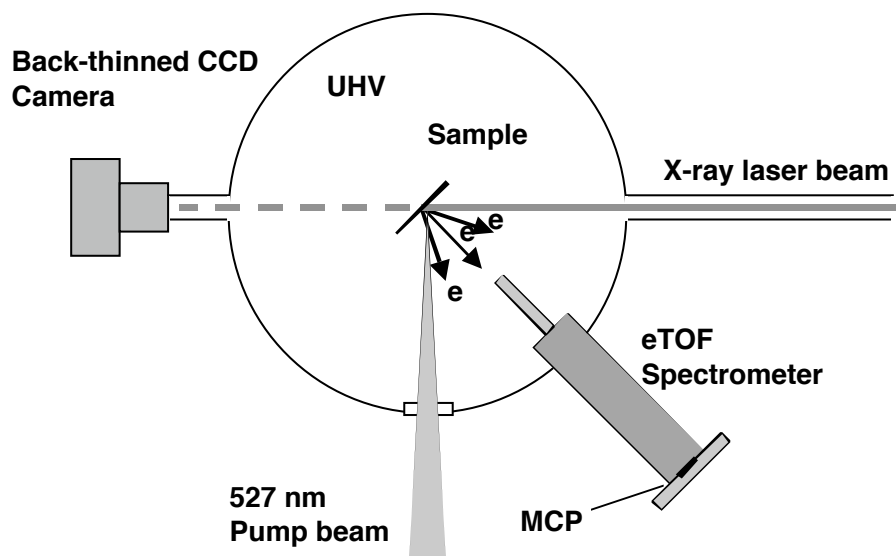


Figure 1. Schematic for the optical pump – x-ray laser probe of material surfaces.

Figure 1 shows a schematic of the x-ray laser photoelectron spectroscopy experimental setup. A fast 400 fs (FWHM), 527 nm wavelength laser pump beam can be focused onto the sample to produce rapid heating and induce phase changes. The x-ray laser probe is collimated by a normal incidence Mo:Si multilayer spherical mirror and relayed along the beamline by a 45° Mo:Si multilayer flat mirror. The narrow reflectivity window of the mirrors selects the x-ray laser wavelength and minimizes other plasma x-rays reaching the sample. A pinhole or thin filter isolates the beamline from the experimental ultra-high vacuum (UHV) chamber, operating below 10^{-8} mbar pressure. The x-ray laser probes the

material surface being heated by the optical laser pump, at various times and induces photoemission. These low energy photoelectrons, with K.E. < 84.5 eV, emitted from the valence band and shallow core levels are detected by the e-ToF spectrometer, the operation of which is described in detail elsewhere. [15] The signal is acquired and digitized using a fast 6 GHz oscilloscope.

3. RESULTS AND DISCUSSION

Figure 2 presents the static x-ray laser induced photoemission e-ToF photoemission spectra for the Ge (100) crystal illuminated with $10^8 - 10^9$ x-ray laser photons. Space charge effects were not evident at these intensities. Each spectrum represents the average sum of two to four shots and the retard (or drift) potentials were varied as shown on each spectrum to improve time resolution and consequently energy resolution. The x-ray prompt peak seen in the spectrum with no drift voltage is generated from scattered x-rays off the Ge surface hitting the micro-channel plate (MCP) detector a distance of $L = 43.75$ cm away. [15] The x-ray prompt peak occurs $L/c = 1.46$ ns after the x-ray laser hits the sample, where c is the speed of light, and can be used as a timing fiducial. These spectra are more indicative of a Ge-oxide layer in the absence of sputter ion cleaning due to the ~ 1 nm mean escape depth of the photoemitted electrons.

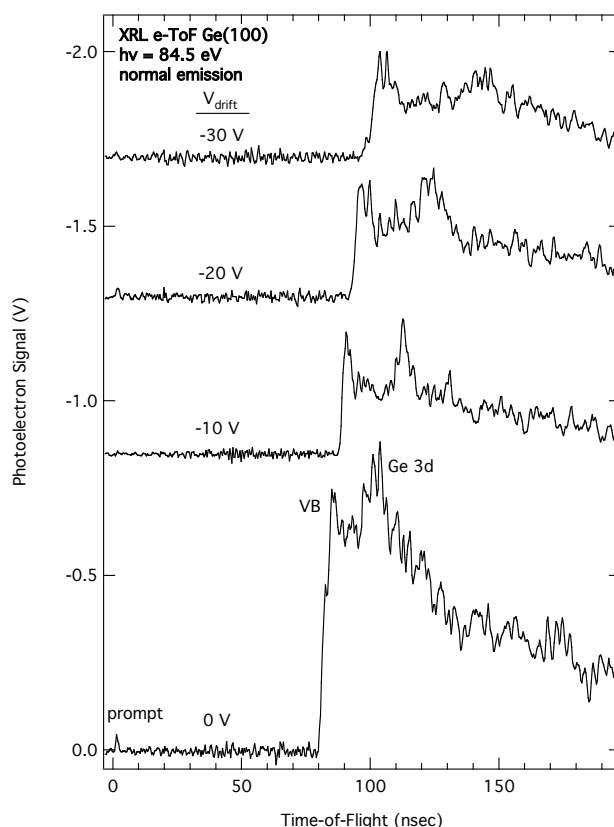


Figure 2. X-ray laser induced photoelectron spectra for Ge(100) surface using various drift voltages.

The upper valence band of oxidized Ge is composed primarily of Ge $4p$ occupied states that hybridize with O $2p$ states. [16] The work function for Ge (100) is 4.8 eV and thus the kinetic energy for these valence band photoelectrons, the first e-ToF event, will be ~ 79.7 eV. The kinetic energies of the Ge $3d_{5/2,3/2}$ spin-orbit pair are 50.5 eV and 50.0 eV, respectively, and are the next expected event in the spectrum. In addition, the photoionization cross-sections for the Ge $4p$ valence band and the Ge $3d$ shell at an excitation energy of 80 eV are 0.039 Mb and 6.999 Mb, respectively [17] which would imply that the strongest peak should be the Ge $3d$ core. However, oxidized Ge has an O $2p$ component in the valence band with a photoionization cross-section of 2.064 Mb at an excitation energy of 80 eV. Therefore, based on the observed peak height ratios for valence band and Ge $3d$ core-level emission, the spectra are indeed indicative of an oxidized surface layer. Non-equilibrium occupation of the valence band states created by the x-

ray laser intensity (10^6 W/cm^2) may also contribute to the unusual electron energy distribution at the valence band edge. The broad background under the Ge $3d$ peak originates from secondary electron emission that represents elastically and multiply scattered electrons.

As we increase the negative drift voltage in the flight tube of the e-ToF analyzer and thus reduce the kinetic energy of the photoemitted electrons, the valence band threshold and separation between the valence band and core-level events change (Fig. 2). The notable decrease in photoelectron signal for the -30 V retarding field is due to a decrease in the effective solid angle of photoelectrons reaching the MCP detector. [18] In the case of no drift voltage, the photoelectron yield as given by $N_p = F\sigma n\lambda T$ can be estimated from the x-ray fluence on the sample after filter and mirror losses ($F = 10^9$ photons/pulse), the Ge $3d$ photoionization cross-section ($\sigma \approx 7.0 \times 10^{-18} \text{ cm}^2$), the Ge number density ($n = 4.4 \times 10^{22} \text{ cm}^{-3}$), the escape depth ($\lambda = 5 \times 10^{-8} \text{ cm}$), and the angular collection efficiency of the MCP detector ($T = 2.5 \times 10^{-4}$). Therefore, we can expect 3.9×10^3 photoelectrons/pulse to arrive at the MCP detector and produce signal. We observe single-shot photoelectron signals in the range of 200-400 mV without retarding.

We now apply this demonstrated capability to the time-resolved examination of changes in the electronic structure of Cu undergoing ultrafast isochoric laser heating. The ultra-thin Cu target consists of 50 nm Cu on a 20 nm C support. X-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemistry of the ultra-thin Cu foil prior to the dynamic pump-probe experiments. Figure 3(a) shows the survey spectrum and the high-resolution Cu $2p$ core-level spectrum for the as received surface. Carbon, oxygen, and nitrogen contamination are evident in the foil. The Si contamination is due to the mounting procedure.

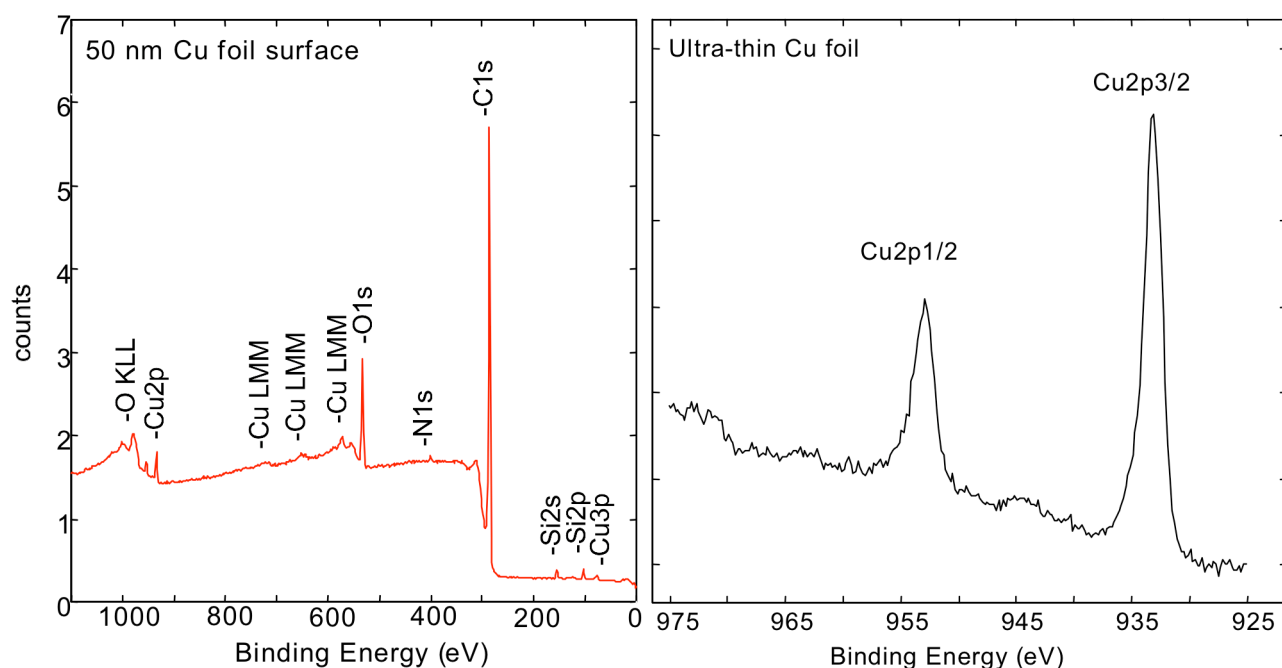


Figure 3. (a) XPS survey spectrum and (b) high-resolution Cu $2p$ core-level spectrum of ultra-thin Cu foil.

Examination of the Cu $2p$ line-shape reveals no plasmon loss features indicative of CuO. [19] However, the nanocrystalline Cu could possibly be preferentially oxidized at the grain boundaries and on the surface as Cu_2O . Nevertheless, these oxides were easily reduced using ultraviolet light prior and during x-ray laser induced photoelectron spectroscopy. [20, 21]

Figure 4 presents the single-shot e-ToF photoemission spectra of the $3d$ valence band of static and laser heated ultra-thin polycrystalline Cu foil illuminated with $10^8 - 10^9$ x-ray laser photons. This sample is sufficiently thin to observe the transmitted x-ray laser beam simultaneously with the photoelectron signal. Again the x-ray prompt peak can be used as

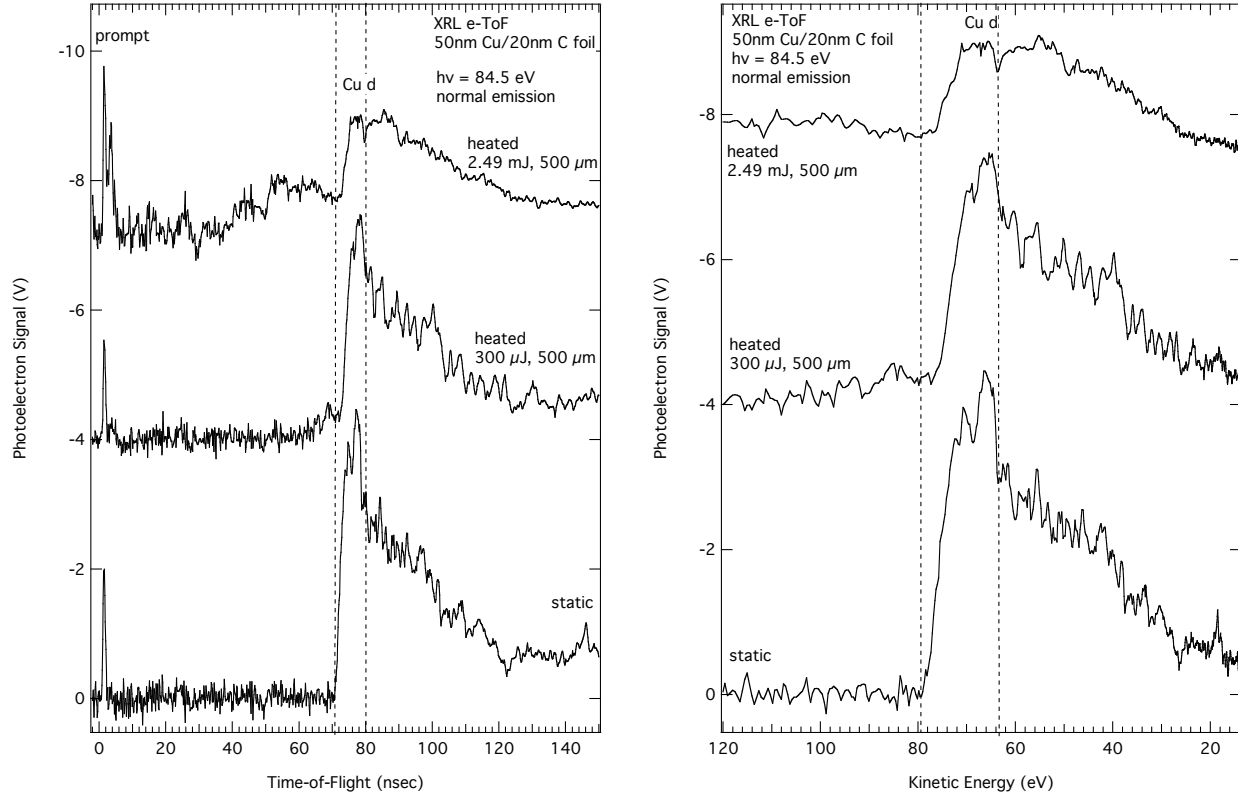


Figure 4. Single-shot x-ray laser induced photoelectron spectra for static and laser heated ultra-thin polycrystalline Cu foil (a) signal versus time-of-flight and (b) signal versus kinetic energy. Dashed lines represent limits of photoemission threshold and Cu *d* band emission.

a timing fiducial. This scattered signal intensity is also sensitive to the surface finish of the sample. The mean escape depth of the photoemitted electrons is on the order of ~ 1 nm for this kinetic energy. In addition, the photoelectron yield as given by $N_p = F\sigma n\lambda T$ can be estimated from the x-ray fluence on the sample after filter and mirror losses ($F = 10^9$ photons/pulse), the Cu *3d* photoionization cross-section ($\sigma \approx 8.7 \times 10^{-18}$ cm²) [17], the Cu number density ($n = 8.4 \times 10^{22}$ cm⁻³), the escape depth ($\lambda = 5 \times 10^{-8}$ cm), and the angular collection efficiency of the MCP detector ($T = 2.5 \times 10^{-4}$). Therefore, we can expect 9.1×10^3 photoelectrons/pulse to arrive at the MCP detector and produce signal. We observe photoelectron signals with amplitudes of 2-4 V with a single x-ray laser shot and without the application of a retarding field.

Under static conditions (lower spectrum Fig. 4) the *3d* valence band electrons will have the highest kinetic energies as governed by $E_k = h\nu - E_b - \phi$, where $h\nu$ is the energy of the incident photon (84.5 eV), E_b is the binding energy of the photoelectron relative to the Fermi level and ϕ is the work function of the material ($\phi = 4.6$ eV for Cu). Valence band photoemission will thus be the first and strongest event in the e-ToF spectrum. The strong Cu *d*-state emission observed at the valence band maximum, i.e. first e-ToF event is indicative of a high density of states (filled *d*-states) that are 2 eV below the Fermi level. [22] The strong emission corresponds to direct transitions from *d*-like occupied bands to unoccupied bands above the Fermi energy. The initial as well as the final states determine the appearance, position, and intensity of these structures, and strongly depend on the applied photon energy. Non-equilibrium perturbations of the valence band states created by the x-ray laser irradiance (10^6 W/cm²) also contribute to the unusually abrupt electron energy distribution at the valence band edge. Displaying the ambient x-ray laser induced Cu valence band photoemission spectrum versus kinetic energy (Figure 4(b) lower spectrum) yields an energy distribution curve that is qualitatively comparable to Cu valence band photoemission spectra presented in the literature [23] that were acquired using synchrotron radiation.

4. CONCLUSIONS

We have successfully validated x-ray laser induced time-of-flight photoemission by measuring the valence band and shallow core-level photoemission in room temperature bulk materials. We have also successfully demonstrated the optical pump-x-ray laser probe characterization capability to observe the evolution of changes in the electronic structure of laser heated ultra-thin metal foils with picosecond time resolution. Single-shot spectra have been achieved showing that the incident photon number is more than enough for these applications. We will further investigate and characterize the range of x-ray laser intensities on the sample and the effect of space charge on the nonequilibrium electron energy distribution in future studies.

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